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Published in:
Physical Review B

Link to article, DOI:
10.1103/PhysRevB.24.2263

Publication date:
1981

Document Version
Publisher's PDF, also known as Version of record

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Angle-resolved photoemission from Au(112)

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(Received 5 November 1980)

The angular variations of the spectral positions of peaks in angle-resolved photoemission spectra for Au(112) due to bulk interband transitions have been calculated using a band model for gold which agrees with other optical data. The calculations agree with the experimental results published recently by Heimann *et al*.

Numerous results of large-angle photoemission experiments on the noble metals have been quite successfully interpreted[1-7] in terms of bulk band-structure models, which simultaneously in general appeared to explain data extracted from other optical experiments. These conclusions, which were drawn from comparisons between calculated spectra and photoemission spectra obtained for polycrystalline samples, seemed well founded a decade ago, and discrepancies between theory and experiment usually did not exceed a few tenths of an electron volt. Recent high-resolution angle-resolved photoemission (ARPE) experiments[8] have, however, seriously questioned the validity of earlier interpretations. The ARPE results obtained by Heimann *et al.*[8] for Au(112) indicated that the final states reached by the photoexcitation processes lie more than 3 eV above the calculated[7,9] final-state band. This discrepancy was very astonishing since the difference in *energy* resolution between the older angle-integrated and the new ARPE experiments is not sufficient to explain why such disagreements were not detected earlier. Consequently, the large discrepancies cannot be attributed to many-body correcting effects or drastic errors in the band models.[6,7,9] Rather it appears that they have been introduced in the interpretation of the angular variations observed in the ARPE spectra. It has been shown elsewhere[10] that the so-called energy-coincidence method (ECM), originally proposed by Kane,[11] is not sufficiently accurate in cases where the initial-state bands are flat as in the noble metals. It follows from Ref. 10 that the energies of the initial state in the *optical transition* related to a specific peak in the ARPE spectrum must be located with an accuracy which is better than $\approx\frac{1}{10}$ of the linewidth at half maximum if the ECM is to be applied in the case of gold. Therefore we find that the ECM cannot be safely applied to the analysis on ARPE spectra for the noble metals, at least not until a detailed line-shape model exists. It is the purpose of the present communication to demonstrate that the data of Heimann *et al. do* in fact agree with a band model which does not involve the very drastic upshift of band 7 (the final-state band considered here) by ≈ 3 eV.

We are well aware that the relevant final-state band (band 7) is *not* correctly predicted by the original[7,9] relativistic augmented-plane-wave (RAPW) calculation when compared with other optical experiments. This is clearly seen by comparing the calculated value (3.8 eV) of the L gap ($L_2' - L_1$, single-group notation) with the values 4.5–4.6 eV found in thermo- and piezo-modulated[12,13] optical experiments. It follows that an upshift of the calculated band by ≈ 0.8 eV is sufficient to obtain a band model which agrees with modulation experiments at L. It should be noted, in this context, that the experimental final-state band along the symmetry line Λ in Fig. 3 of Ref. 8 when extrapolated to L leads to an L gap of ≈ 6 eV, i.e., far too large when compared with other optical experiments. As discussed elsewhere,[14] the position of the top of the d bands relative to the Fermi level as obtained in the RAPW calculation[7,9] agrees with the observed *main* interband edge (2.38 eV). Although it is not clear whether the band model of Refs. 7 and 9 needs to be adjusted also at Γ far above the Fermi level, we shall in the present analysis use a band model which differs from the original one[7,9] *only* by having the final-state bands (band 7 and higher bands) rigidly upshifted by 0.8 eV.

Figure 1 shows the calculated angular variations of the initial-state energies of the optical transi-

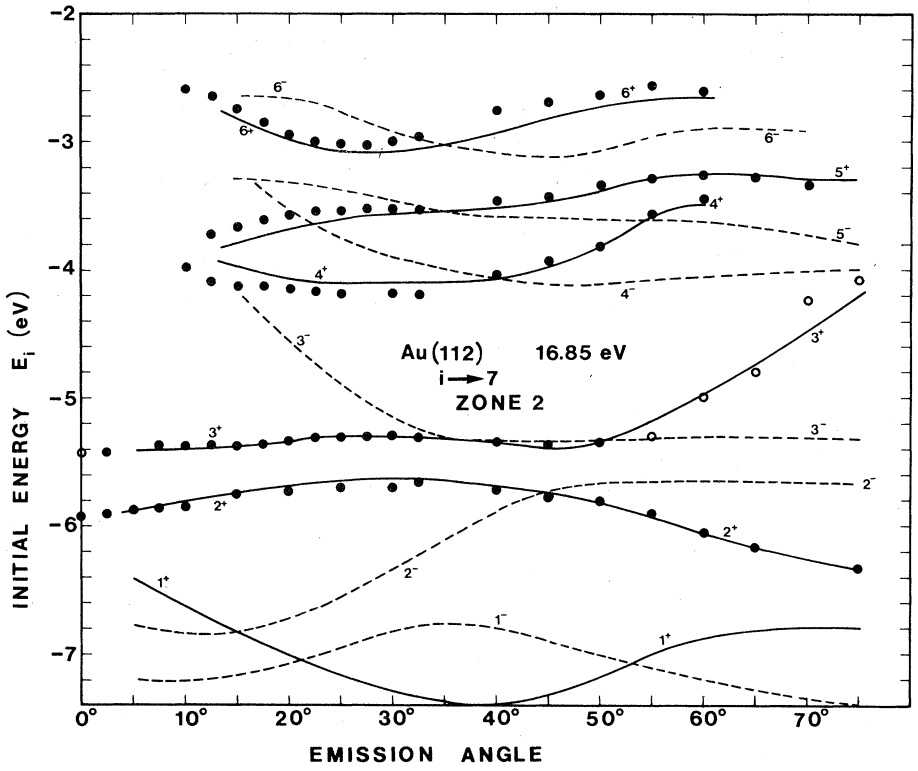

FIG. 1. Initial-state energies (zero at the Fermi level) of transitions from bands numbered $i=1$ to $i=6$ to the final-state band, band 7. Curves shown with a full line refer to optical transitions where the group velocity in the final state has a component toward the surface, the (112) crystal face. Dashed curves represent calculations where the final-state group velocity is directed toward the interior of the crystal. The dots represent the energies of the experimental peak positions (Ref. 8). We have, however, reduced all experimental binding energies by 0.35 eV. The open circles correspond to weak shoulders in the experimental spectra. The emission angle is measured from the surface normal towards [110]. The calculations assumed the work function to be 4.69 eV.

tions to band 7. Only second-zone final states are considered. The curves shown represent the initial-state energies of the optical interband transitions as a function of the detector position. This position is specified by the emission angle, which is measured from the surface normal, [112] toward [110]. The calculated curves are obtained from the band model assuming that the component of the wave vector parallel to the surface is conserved during emission, and the work function of the (112) surface is taken[8] to be 4.69 eV. The curves in Fig. 1 shown with a full line represent those second-zone transitions where the final-state group velocity has a component *toward* the *surface* (this is also indicated by the superscript + to the initial-band numbers). The dashed curves, on the other hand, relate to transitions where the final-state group velocity is directed *toward* the *interior* of the crystal. The dots show the initial-state energies of peaks in the experimental[8] ARPE spectra. The experimental binding energies have, however, all been reduced[15] by 0.35 eV. It is obvious from Fig. 1 that the agreement between the experimental peak positions and the calculation is so close over the entire range of emission angles that we can conclude that the band model suggested here relates very well to the experiments of Ref. 8. The ARPE experiments for the (112) surface are particularly well suited for this analysis since the {112} planes are *not* mirror planes of the fcc lattice. Therefore the + curves and − curves (full lines and dashed lines, respectively, in Fig. 1) are not degenerate. It is seen that the experimental points all follow the calculated + curves.

Figure 2 shows the angular variation of the $6 \rightarrow 7$ transitions (final-state group velocity directed towards the surface) after a slight readjustment[15,16] of the shift applied to the experimental binding energies. It should be emphasized that the experimental points give peak positions in the ARPE spectra whereas the calculation gives the energy below the Fermi level of the initial state involved in the optical transition. Even disregard-

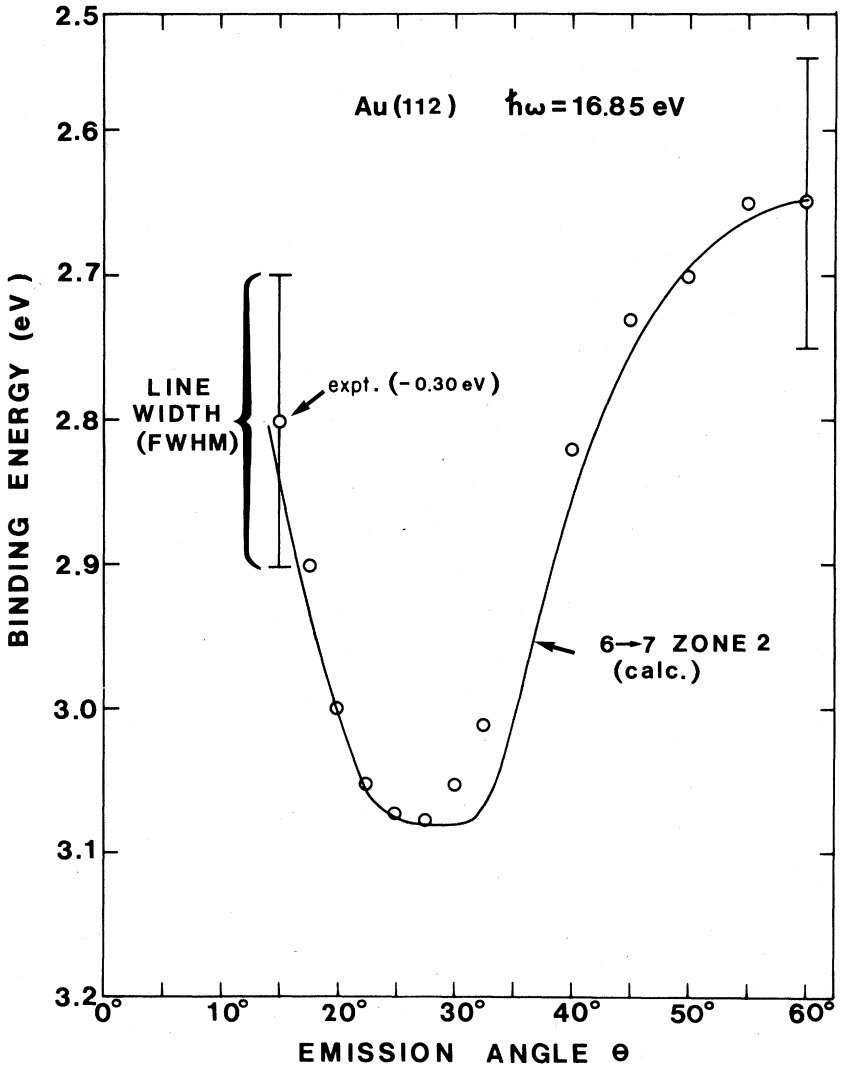

FIG. 2. Angular variation of the 6→7 transition (full line) as calculated from the band model. The circles represent experimental (Ref. 8) peak positions (binding energies reduced by 0.30 eV). An estimate of the linewidth, full width at half maximum (FWHM), is indicated.

ing possible many-body corrections we are not able, at present, to *calculate* the peak position itself directly from the band model. This may differ somewhat from the energy of the transition due to surface effects and matrix element variations, and since the finite acceptance angle of the detector implies an integration over a small but finite volume in $\vec{k}$ space. Thus, as long as a detailed line-shape analysis cannot be carried through we assume that the experimental initial-state energy of the transition is within range of the order of magnitude of half the linewidth (FWHM in Fig. 2) around the peak position.

In spite of minor reservations taken in the analysis above it is shown that the (112) ARPE data for gold as obtained by Heimann *et al.*[8] relate extremely well to a band model which simultaneously agrees with other optical experiments. This band model differs from the RAPW calculation[7,9] by having band 7 upshifted by 0.8 eV. This result is of importance as it demonstrates that ARPE is well suited for measuring optical band structures, and further it follows that the new high-resolution experiments, which contain a wealth of detailed information, do not invalidate the interpretations of the older, angle-integrated experiments as far as bulk band contributions are concerned.

The present work was supported by the Danish Natural Science Research Council.

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